

Desphosphorization in ironmaking and oxygen steelmaking

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Abstract

Steelmaking is an extensive industry based on modifying the physical properties of iron to fit a wide range of applications by either adding alloying elements or removal of impurities. Thus, the effects of various elemental components on final steel properties are at the heart of the steelmaking process whether in small concentrations coming from the raw materials or being in larger concentrations as alloying elements. Owing to increased demand of iron ore raw materials, the access to high-quality ores has been under stress and thus, increased usage of low-quality ores, which contains high concentrations of impurities such as phosphorus and sulphur has become more economical. Such impurities have been known to have adverse impacts on the final steel properties and need special management in conventional steel making operation. This report primarily focuses on the management strategies of phosphorus in steelmaking including the behavior of phosphorus and its removal strategies in several core components of the process: blast furnace (BF), basic oxygen furnace (BOF), electric arc furnace (EAF) and argon oxygen decarburization (AOD). The objective of the report is to review underlying research in the area giving a reference to the available literature and support propagation of future research projects addressing various aspects of dephosphorization in steelmaking.

Nomenclature

Symbol/Abbreviation	Significance
AOD	Argon Oxygen Decarburization
ASS	Air-cooled Steel Slag
BF	Blast Furnace
BOF	Basic Oxygen Furnace
BOS	Basic Oxygen Steelmaking
CAS-OB	Composition Adjustment by Sealed argon bubbling with Oxygen Blowing
CRK	Chromium converter
DRI	Direct Reduced Iron
EAF	Electric Arc Furnace
GBS	Granulated Blast-furnace Slag
GGBS	Ground Granulated Blast-furnace Slag
HM	Hot metal
LD	Linz and Donawitz converter
RHS	Right hand side
SAF	Submerged Arc Furnace
SSAB	Svenskt Stål AB (Swedish Steel)
[]	Concentration in hot metal
()	Concentration in slag
f	fugacity
a	Henrian activity

1. Introduction

Steelmaking process, around the world, primarily relies upon two main raw materials, iron ore and coke (or coal) which constitute the two major components of the steel: iron and carbon. However, there many types of steel specialized for various applications requiring unique properties such as toughness, hardness, ductility, anti-corrosion etc. These properties can be fine-tuned by adjusting the content of other major (including C, Cr, Ni) or minor components (such Mn, Ti etc.) in steel which interact both with each other and with iron to obtain the desired properties. These additional elements come into the steel making process in three ways: as impurities in the iron ore and coal; added intentionally as additives; or as carryover along with additives from their ores or respective sources. For example, chromium is often added to steel to make it more resistant to corrosion and thus, making stainless steel used in most common steel applications. This is often achieved by adding carbon-chromium ore which often brings along traces of carbon, sulphur, phosphorus, titanium and silicon. Some of these additional components are desirable based on the type of steel and type of the process for example silicon often helps raise the temperature in steel making with the exothermic oxidation while others are undesirables for example excessive carbon, sulphur, and phosphorus. A list of various components added to steel and their impacts on final steel properties will be listed in Table 4. Thus, the steel industry needs to make fine adjustments with careful control of various additives and process parameters to obtain the desired steel quality.

Steelmaking involves primarily two major pathways: 1) basic oxygen steel making (BOS) 2) the direct iron reduction (DRI) with electric arc furnace (EAF) pathway. Almost 66% of the worldwide steel is produced by BOS pathway while the rest use a combination of the DRI and EAF pathways [1]. In BOS pathway, the iron ore is primarily reduced by coke in a blast furnace (BF) where the coke also produces heat for the reactions by oxidation from atmospheric oxygen and iron oxide. The hot metal from the BF needs to be further purified and the various impurities need to be adjusted to a required composition for the application. Especially owing to the decrease in feed ore quality with limited resources available, it is getting more important to adjust impurities while considering the process economics and performance. In the hot-metal (HM) by this point, some of the impurities are already significantly removed for example sulphur, 60% of which is coming from coke the rest in additives and iron ore, is significantly (around 80-90%) removed in BF as slag while the rest remains in HM [2]. However, there are still other impurities which are in HM in significant proportions which need to be removed for example phosphorus, 70% of which is coming from iron ore with only around 20% coming from coke [2], almost 95% of it ends up in HM after BF. These components which are undesirable or need adjustment are either processed through HM pre-treatment processes such as in torpedo vessels in Japan [2] or directly input into a basic oxygen furnace or converter with or without recycled steel scrap. In the converter, oxygen is blown into the metal bath at high temperature to remove an effectively significant portion of carbon as gases while phosphorus, silicon and some other components as slag formed from flux (a mixture of lime and other additives). The crude steel obtained from the process is sent to a secondary steel making process by tapping it out into a ladle. Here, the final adjustments to steel are made with addition of alloying elements and de-oxidizers. The resulting steel is sent for casting where it is cast into

steel slabs with minimal further composition adjustments. The overview of the process is shown in Figure 1.

The other important steel making process is the direct iron reduction- electric arc furnace pathway. Here, the iron ore is reduced in the presence of a reducing gas or elementary carbon produced from natural gas or coal. Unlike BF, the reduction process occurs below the melting point of iron in the temperature range of 800 °C -1200 °C. This process has the advantage over BF of having lower cost, high effectiveness in smaller scales, and more environmentally friendly. The major drawback of the process is the limited scalability, and difficulty of removal of gangue from the iron ore especially silicates since large-scale composition cannot be adjusted in DRI. The most important customer of DRI is EAF based steel maker since the DRI is available in solid form as required for EAF operation, furthermore, DRI and EAF can be owned by separate entities and they don't necessarily have to be placed close-by unlike the integrated steel making process (BOS). EAF, as the name suggests, utilizes electric arc to melt the raw feed, which is primarily recycled steel scrap, with the addition of direct reduced iron (DRI) and additional additives can be added to adjust the steel composition [3].

In both of the processes, one of the important impurity to be removed is phosphorus. Section 1.5 details the impact of phosphorus on steel. Usually, the phosphorus content of HM is in the range of 0.4 -1.0% and however, the demand of content in steel is around 0.025% or lower. The main sources of phosphorus in steelmaking are iron ore and coke, while some phosphorus is also added by additives, however, most of the phosphorus is removed either in hot metal pretreatment processes, the converter, and secondary steelmaking.

This report is structured to present a brief overview of role of phosphorus in steel making. In Section 2, the equilibrium of phosphorus is detailed along with a series of developments that have been undertaken to understand the phosphorus distribution between slag and steel. Section **Error! Reference source not found.** addresses some equipment-specific phosphorus behavior with consideration of industrial application and operation.

1.1 Motivation and Scope of the report

The report focuses on various aspects of the role of phosphorus in steel making, its removal techniques at various stages and its improvement pathways. The content of report will lay the foundation of the research aiming at critical areas of interest in dephosphorization, identifying corresponding research questions and research interests of both the university and industrial partners in the project while giving an overview of the processes to be used as a comprehensive reference within the scope of the report. The report scope would primarily include steelmaking process from after the blast furnace till the casting point or before casting. It will include BOS process with converters of various types, variety of blowing techniques, and various slag types as well secondary steelmaking processes with special emphasize on argon oxygen decarburization (AOD) process. The report excludes process prior to blast furnace, downstream at casting and the direct iron reduction processes. However, electric arc furnace without chromium converter technology will also be part of the report scope. The geographical scope of the process will include steelmaking within Europe, and North America, thus, unique processes implemented in East-Asia including Japan and South Asia are beyond scope of this report. The chronological scope of the report will include the processes and

research dating back to last 68 years. Any older process which is no longer in practice in any form is not included in this report. For consideration of industrial application, the phosphorus concentration range within any process would be between 0.01% to max 0.1% thus including the iron ores of wide range of concentrations as well as steel types. However, very high phosphorus concentrations which would require extensive pretreatment before BF or BOF and thus, won't be included since it would require specialized techniques such as torpedo vessel dephosphorization techniques which are not part of basic oxygen steelmaking process inherently.

1.2 Iron and Steel making

Steelmaking is one of the most energy-consuming industries in the world. In 2013, China's steel industry alone constituted 15.9% of the country's total energy consumption and this is increasing rapidly [4]. In 2008, EU produced 14.9% of the total world production; the same number in 2003 was 24.6%. Although the fraction of steel production in the EU is declining, this number is still adding up due to the increased production of steel in China[5]. Steel has been used as a structural material since 3000 BC. Nowadays, steel is produced using Basic Oxygen Furnace (BOF) and Electric Arc (EA) methods. It is produced in a batch process and the reaction mechanism involves the reduction of sulphur, carbon and phosphorus levels by adding other elements such as manganese, chromium, nickel or vanadium to enhance the properties of iron steel [6]. Figure 1. shows the typical iron and steel making.

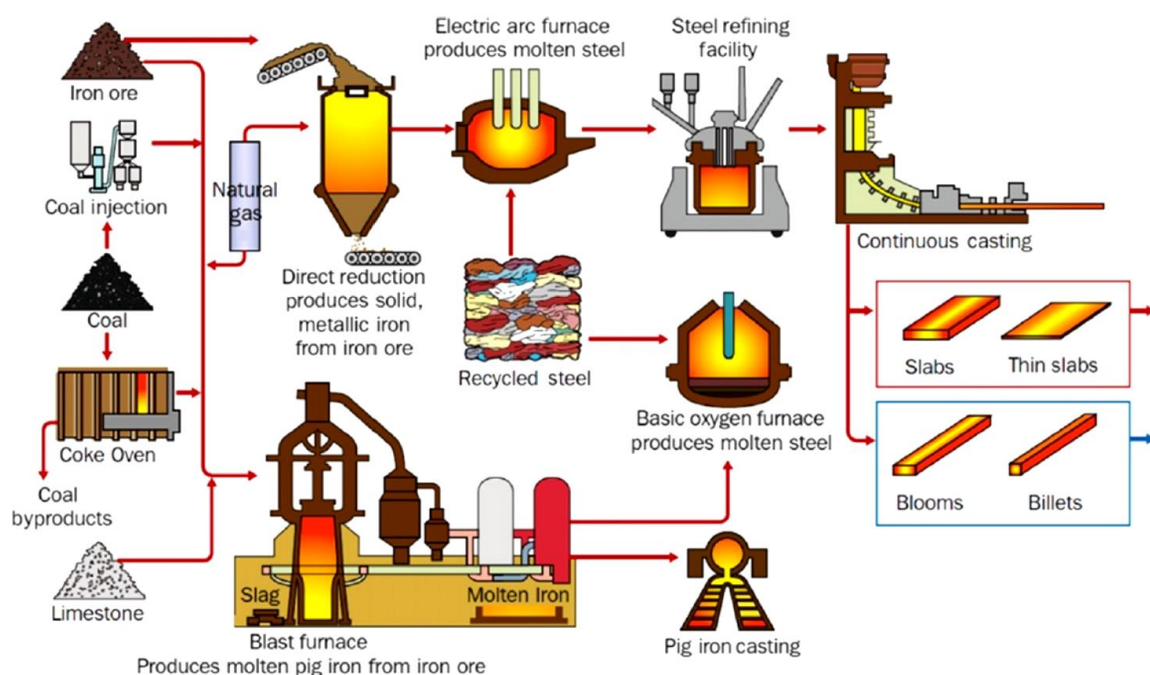


Figure 1. The overview of ironmaking and steelmaking processes

1.2.1 Iron Making in the Blast Furnace

Iron ore, coke, and limestone are charged into the blast furnace and hot air is blown into the blast furnace from the bottom of the furnace to melt iron ore and fluxes at about 1600 °C. The ore is melted and solidified afterwards, at a stage this product is termed as pig iron. All the other impurities other than iron are called slag, which floats on the molten pig iron and solidifies after coming from the blast furnace.

1.2.2 Steelmaking in Converters

All the materials after the slag removal are transported from the blast furnace to the steel melting shop where all the impurities are reduced in the basic oxygen furnace or in an open-hearth furnace. Silicon or aluminum are used as deoxidizers to control the oxygen content. At this stage, there are two grades of steel called killed steel and semi-killed steel having <30 ppm of [O] and 30-150 ppm [O] respectively. Typical structural steel contains carbon (0.10-0.125%), manganese (0.4-0.12%), sulfur (0.025-0.05%) and phosphorus (0.025-0.05%).

1.2.3 Refining for carbon steels and stainless steels

Refining of steel proceeds in order to obtain desired mechanical strength and service life. In the case of stainless steels, it is done by adding 10 to 30% chromium with varying concentrations of nickel, molybdenum, sulfur, niobium, and titanium depending upon the end use. These desired properties are induced in a number of ways such as argon-oxygen decarburization (AOD), ladle treatment and composition adjustment by sealed argon bubbling with oxygen blowing (CAS-OB). Among all process, argon-oxygen decarburization (AOD) process has revolutionized the steel making process because it is cost-efficient, has high productivity and easy to operate [7].

1.2.4 Iron and Steelmaking Slags

Slag disposal is a huge problem to the steel industry, typically, 400 Mt of slag is produced annually worldwide, whereas the EU annual share is almost 50 Mt [8]. Slag produced from the production of iron is known as blast-furnace slag; it is a very useful construction material. The end structure of slag is directly dependent on how it is allowed to cool down when discharged from the blast-furnace, sometimes it is in the aggregate form or a cementitious material. When molten slag is allowed to cool by air then an almost inert, hard, crystalline material can be produced.

BF slags are crushed into aggregates and if allowed to cool rapidly in water, instead of aggregate it forms a vitrified (glassy) material having high hydraulic potential. Latterly, this product is known as granulated blast-furnace slag (GBS), having high natural cementitious properties. This cementitious slag is treated with lime for hard clean granular materials but due to its ‘coarseness’, it has a lower surface area for high effectiveness with ‘dirtier’ or cohesive materials. This problem can be solved by grinding the GBS to produce greater surface area. Due to grinding, the rate of reaction is increased significantly. At this stage, this GBS is called

ground granulated blast-furnace slag (GGBS). This GGBS can use as a core constituent for the production of concrete.

The other slag is obtained is from the steelmaking in the BOF; currently, air-cooled steel slag (ASS) is usually combined with GBS, for the treatment of sands or well-graded combinations of fine and coarse aggregates. This combination has an insufficient surface area for the treatment of fine-grained materials [9].

Chemical compositions of steel slags vary from the type of ore used in the blast furnace for steel making. Typical chemical composition for iron making and steel making slags are shown in Table 1.

Table 1. Chemical Compositions (wt-%) of Iron Making and steelmaking slags by XRF [10].

Constituent	Blast furnace slag	Steel Slag
CaO	35 - 42	35 - 45
SiO ₂	33 - 38	11-17
Al ₂ O ₃	10-15	1-6
MgO	7-12	2-9
FeO	≤ 1.0	16-26
MnO	≤ 1.0	2-6
P ₂ O ₅	-	1-2
S _{total}	1 – 1.5	≤ 0.2
Cr ₂ O ₃	≤ 0.1	0.5-2

1.3 Industrial steelmaking processes

1.3.1 Carbon steelmaking at SSAB Europe Oy

SSAB Europe's steel mills have an annual production capacity of 4.9 million tonnes. The process schematic overall is that SSAB receives rather low phosphorus iron ore and in the blast furnace it is reduced in the presence of coke and flux along with recycled BOF converter slag. The crude hot metal is sent without any further treatment (no info on desulphurization yet) to a converter where additional flux and scrap is added to the hot metal and the primary dephosphorization occurs here where [P] is oxidized to P₂O₅ by iron oxides with additional blowing near the end. The additional blow near the end makes more FeO to float in the flux and thus allowing for additional dephosphorization. Additionally, in the converter, low MgO in BOF slag facilitates the dephosphorization and additional slag splashing is used to reduce wall degradation. No additional special processes are used here, i.e. no MURC, or double slag processes. The liquid yield from the converter is around 90% with heat size of around 102 t, 105 t (vacuum degassed heats) and 120 t (calcium treated). No dolomite is used here, only lime. And the Fe amount in the slag is around 15% while containing 2% of MgO. The net slag mass is typically to 80 kg/tons of steel or 95 kg/hot metal.

Downstream of the converter, the secondary steel making process involves CAS-OB, ladle furnace and degassing tanks. Here aluminum is added to the system to maintain the temperature as well as facilitate alloying with different materials. Additional phosphorus may

come here through the additives. Al_2O_3 is removed by the addition of calcium to the system which forms calcium aluminate. The approximate liquid yield after the process is around 90% so for each 1 t crude molten steel, we get around 0.9 t of steel. The final stage (of interest) is the casting where molten steel is molded into steel slabs. Here two samples are taken at one third of the casting where it enters and two third points in the casting before it goes into the final casting slab. There is no stirring in the ladle during casting and there is no significant increase in the phosphorus content here. The final compositions of elements in steel is shown in Table 2. and approximate calculations of different streams in BOF is shown in Table 3.

Table 2. Final steel properties composition ranges [7]

S.No.	Elements	Composition (wt-%)
1	C	0.003-0.5
2	Mn	0.15-2.7
3	Si	0.025-0.75
4	Cr	0-1.45
5	Nb, Ni, Cu, Mo	Depends on use

Table 3. Approximate calculation for the stream balance of BOF in input and output [11]

Input					
Mass flow(kg/ton of steel)	Hot Metal	Scrap	Ore	Flux	Gas input
	872.24	201.55	11.684	54.8	75.52
Fe	94.19%	99.49%	98.60%	—	—
C	4.68%	0.09%	—	—	—
Si	0.60%	0.02%	1.11%	0.97%	—
Mn	0.45%	0.36%	0.29%	—	—
P	0.06%	0.01%	—	—	—
S	0.01%	0.02%	—	—	—
CaO	—	—	—	87.45%	—
MgO	—	—	—	11.59%	—
O ₂	—	—	—	—	100%
Output					
Mass flow(kg/ton of steel)	Steel	Slag	Fumes	Gases	
	1000	98.83	16.554	100.41	
Fe/(FeO(T))	99.80%	26.73%	100.00%	—	
C	0.04%	—	—	—	
Si / (SiO ₂)	0.01%	12.15%	—	—	
Mn /(MnO)	0.14%	5.06%	—	—	
P/(P ₂ O ₅)	0.01%	1.14%	—	—	
S	0.01%	—	—	—	
CaO	—	48.49%	—	—	
MgO	—	6.43%	—	—	
O ₂	—	—	—	—	
CO	—	—	—	84.91%	
CO ₂	—	—	—	14.83%	

1.3.2 Stainless steelmaking at Outokumpu Stainless Oy

The production capacity of Tornio works is around 1.7 million tons cast slabs annually. The steel melting shop consists of two lines, the charge weight of line No.1 is 95 tons and of line No. 2 150 tons. The specialty of line 1 is a chromium converter for treating liquid Ferrochrome from the Ferrochrome melting shop (Outokumpu Chrome Oy). The stainless steel production is mostly scrap based and begins at the raw material yard. The raw materials are melted in an electric arc furnace (EAF). After melting, the liquid steel is charged in an Argon Oxygen Decarburization converter (AOD) to reach the final quality of the steel. The AOD No.1 is charged with liquid ferrochromium from the chromium and molten steel mixture of oxygen and an inert gas, as argon and nitrogen are injected into the melt. Carbon content in the melt is reduced to specified limits and the desulphurization process is reducing the sulphur content. Between the AOD batch process and continuous casting is a ladle station one for each line for adjusting the steel quality to final limits. Special alloy elements may also be added at this stage and the melt is homogenized by argon injection. The required temperature for the continuous casting machine is adjusted at the ladle stations.

After the ladle treatments, the melts are transferred to the continuous casting units. The melt is solidified and torch cut into 800-1620 mm wide slabs. Most of the slabs are transferred when still hot from the continuous casting units to the hot rolling mill. Prior to hot rolling, possible surface defects are removed by grinding. Two of the four grinding machines are able to grind hot slabs. The hot rolling mill is able to roll the slabs to a black hot band with a thickness of a few millimeters. The 14 meter long steel slabs are first rolled to 22 mm thickness in the roughing mill. The finishing is made in a Steckel-type finishing mill with a maximum rolling speed of 600 m/min. Leader strips are welded to the beginning stages. The black hot strips are first softened or annealed in the annealing furnace. The cold rolling is carried out in reversible Senzimir mills. The final product is cut in specific dimension in sheets or coils [12]. The schematic diagram of production of steel at the Outokumpu is shown in Figure 2.

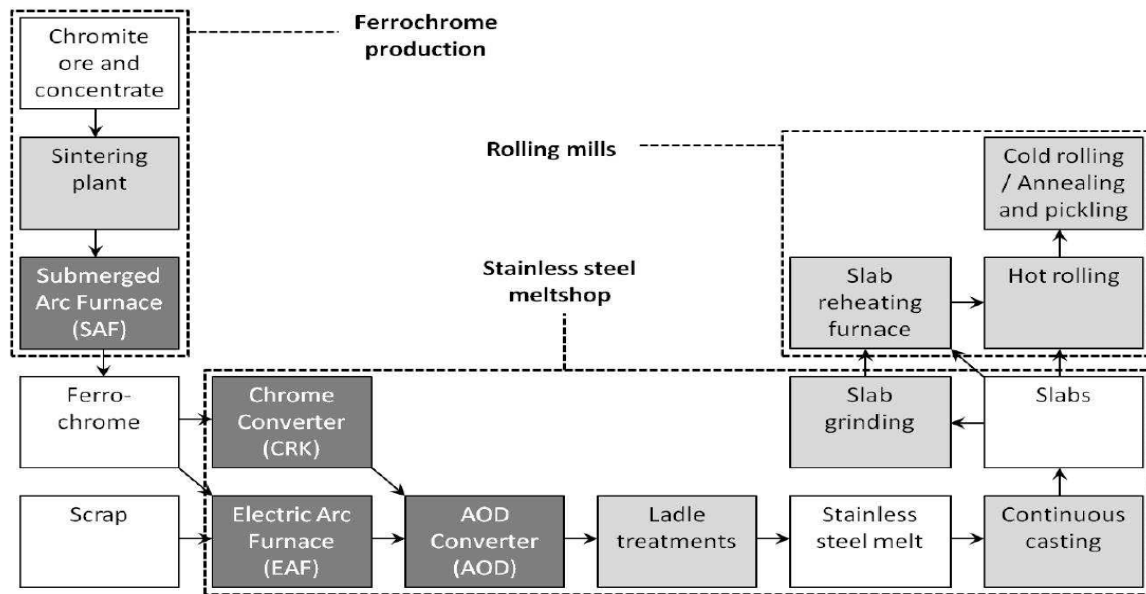


Figure 2. Schematic presentation of the stainless steel production at the Outokumpu Chrome and Outokumpu Stainless Tornio Works

1.4 Impact of alloying elements

The physical properties of steel are heavily influenced by the presence of various elements, their compositions and their interaction with iron or each other. Many of the elements come into steel either from the raw materials or from additives and their compositions are finely adjusted to get the desired properties of steel. Materials such as carbon, manganese, and titanium improves strength and toughness of steel while tungsten, molybdenum and cobalt add high-temperature resistance. Corrosion resistance is also dependent on materials such as chromium, copper, the galvanized layer of zinc, and even phosphorus. However, most of the materials of their own set of negative impacts too for example phosphorus makes steel more brittle. Additionally, different substances also interact with each other in different proportions for manganese increases machinability in presence of sulphur because of formation of manganese sulphide. Table 4. lists some impacts of important alloying elements on final steel.

Table 4. Impact of alloying elements [13], [14]

Elements	Concentration (%)	Positive aspects	Negative aspects
Al	0.95-1.30	Produces finer grains and improves toughness	Lowers forging quality
B	0.001-0.003	Added to small quantities to have a hardening effect	
C	0.003-0.42	Improves hardenability and strength	
Cr	0.5-18	Improves hardenability, strength, response to heat treatment and wear resistance	Reduces ductility, forgeability and machinability
Co	14 max	Strength and hardness at high temperatures and magnetic permeability	
Cu	0.1-0.4	Precipitation hardening properties and increase corrosion resistance.	
Mn	0.25-13	Improves hardenability, and wear resistance. Also increases machinability in combination with sulphur	Decreases ductility and may cause embrittlement at high conc. At too low conc. it may promote porosity and cracking
Mo	0.2-5.0	Increases hardenability and strength, particularly at high temperatures. Improves corrosion resistance and creep strength	
Ni	2-20	Increases strength, impact strength and toughness, corrosion resistance and hardenability	
P	0.03-0.10	Increases the tensile strength of steel along with improving machinability and corrosion resistance	May cause embrittlement at higher conc. and decrease toughness
S	0.08-0.35	Improves machinability	
Si	0.2-1	Improves strength and hardness and facilitates good galvanized layer formation	
Ti	0.25-0.60	Improves both strength, toughness and corrosion and heat resistance	may cause embrittlement during thermal stress relief treatments
V	0-0.15	Increase strength at high temperatures and ductility can be retained. Increases hardenability, fracture toughness, wear resistance, and heat resistance	
W	10-20 Max	High hardness and strength at high temperature, and heat resistance.	

1.5 Impact of Phosphorus in Steel

The effects of phosphorus (P) on the properties of steels are summarized in the Table 5. It can be seen that P has both positive and negative effects on the steel's properties.

Table 5. Effects of phosphorus on properties of steels

S.No.	Property	Effect of phosphorus
1	Strength	Strong positive (strengthens ferrite)
2	Bake hardenability	Positive
3	Ductility	Strong negative
4	Galvanic annealing	Can improve resistance to powdering
5	Phosphatability	Positive
6	Enameling:	
	a) Fish Scaling	Negative
	b) Pickling	Positive
7	Weldability	Not harmful for contents less than 0.1 %
	Core loss in motor	
8	lamination	Strong negative
9	Fracture toughness	Strong negative

The low phosphorus content is necessary for high ductility such as in thin sheets, drawn steel and pipelines etc. Owing to the rising prices of iron ore, usage of cheaper high P iron ore is increasing which requires additional consideration for dephosphorization for such applications.

Phosphorus spread within the steelmaking process owing to the recycling of BOF slag for disposal in order to retrieve iron and lime content in the slag and minimize slag disposal. A significant portion of the dephosphorization happens during the primary steel making, especially in the basic oxygen furnace process. The process improvement, in general, involves a better understanding of phosphorus equilibrium between metal-slag interface, its thermodynamics and kinetics of the phosphorus partition reaction [15].

1.6 Phosphorus distribution flow and Sankey-diagram

Phosphorus balance in each stage of BF and BOF is shown in Table 6. and Sankey diagram is shown in Figure 3.

Table 6. Typical phosphorus distribution between BF and BOF

BF				BOF			
In	kg/ton of steel	Out	kg/ton of steel	In	kg/ton of steel	Out	kg/ton of steel
Iron ores	0.528	Hot Metal	0.6049	Hot Metal	0.6049	Slag	0.6223
Coke + Coal	0.122	Slag	0.0325	Scrap	0.0874	Steel	0.07
		Dusts	0.0060				
		BF Sludge	0.0065				
Total input	0.65	Total output	0.65	Total input	0.6923	Total output	0.6923



Figure 3. Sankey-type diagram of the phosphorus distribution flow for a standard steel grade. Arrows represent the amount of phosphorus present in a flow, necessary for one tonne of produced steel.

Phosphorus balance in each stage of EAF and AOD is shown in Table 7. and Sankey diagram is shown in Figure. 4.

Table 7. Typical phosphorus distribution between EAF and AOD

EAF				AOD			
In	kg/ton of steel	Out	kg/ton of steel	In	kg/ton of steel	Out	kg/ton of steel
Scrap	0.2	Slag	0.0029	Crude steel	0.29	Slag	0.22
Flux	0.09	Steel	0.2871	Additive	0.02	Steel	0.09
Total input 0.29 Total output 0.29				Total input 0.31 Total output 0.31			

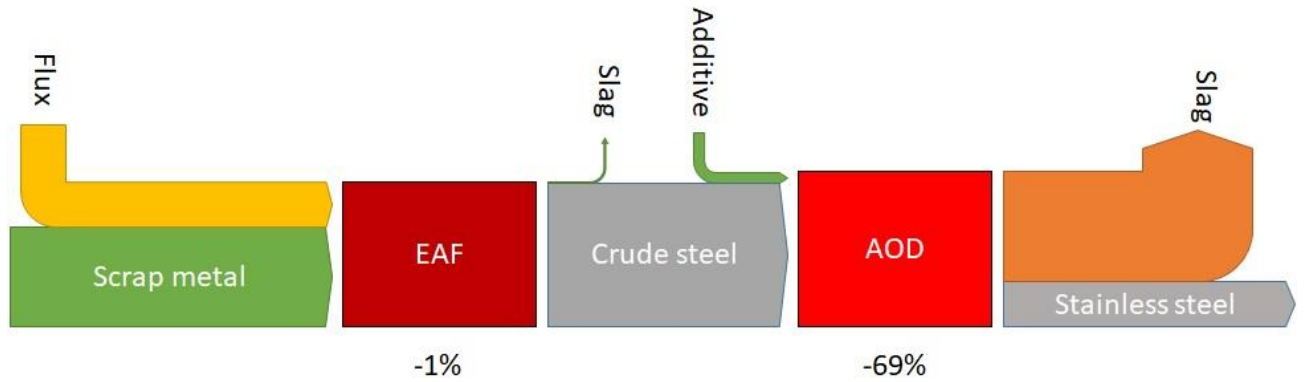
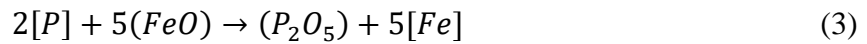
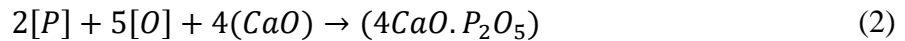


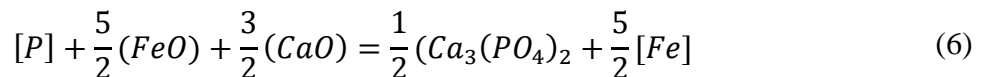
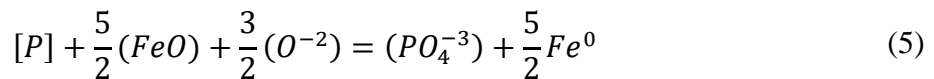
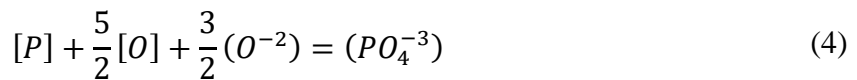
Figure 4. Sankey-type diagram of the phosphorus distribution flow for a standard steel grade. Arrows represent the amount of phosphorus present in a flow, necessary for one tonne of produced steel.

2 Behaviour of Phosphorus in Ironmaking and Steelmaking

Over the course of development of experimental research on dephosphorization, several forms of chemical reactions were proposed to describe the transfer of phosphorus between metal and slag. Early researches [16]–[18] described a series molecular representations for the dephosphorization reaction:



Here, [X] represent species in metal phase while (Y) represent species in slag phase. The validity of such relations were questioned over time and consequently, ionic representation of the reaction were proposed [19], [20].



Regardless of the equation used, the three main understandings from the equations are:

1. High slag basicity is required to accept phosphorus from metal to slag
2. A high oxygen potential must exist to drive phosphorus from the metal to slag
3. Low temperature promotes thermodynamics of phosphorus removal.

A large number of equilibrium correlations have been developed and improved to indicate the phosphorus concentration dependency on various species in slag. The earliest examples of such studies were done in the 1940's indicating the dependency on slag basicity especially CaO and FeO concentrations where they noticed an increase in dephosphorization with an increase in concentration [16], [17], [21]. Turkdogan and Pearson [18] however, argued that the methods of calculating the reactant concentration doesn't represent their actual activities in the system and thus won't hold if the conditions are changed. They instead proposed taking the reaction in simplest form indicated by Eq. 1 [18].

Based on this they evaluated the activity coefficients and observed that silica increased the activity coefficient of P_2O_5 while the basic oxides such CaO and MgO decreased it. Later Suito et al. [22], [23] explored in detail a slag system involving CaO-SiO₂-MgO-FeO_x in MgO crucibles and concluded that phosphorus distribution ratio increased with increasing content of CaO in slag and with decreasing temperature. They also observed that CaF₂ has almost the same effect as CaO without raising the slag melting point. Additionally, they observed the CaO equivalency of Na₂O and BaO of 1.2 and 0.9 on weight percent basis. Another important finding was the impact of MnO on the dephosphorization partition ratio, it was observed that higher MnO concentration tend to decrease the phosphorus partition ratio. They proposed a distribution ratio correlation which was later modified by Ide and Fruehan [24] as:

$$\log \left(\frac{\%P}{[\%P](Fe_t)^{\frac{5}{2}}} \right) = 0.720[(\%CaO) + 0.15(\%MgO) + 0.6(\%P_2O_5) + 0.6(\%MnO)] + \frac{11570}{T} - 10.520 \quad (7)$$

Where

$$\%Fe_t = \frac{\%Fe_tO}{1.286} \quad (8)$$

$$\%Fe_tO = \%FeO + 0.9 \%Fe_2O_3 \quad (9)$$

However, Lee and Fruehan [25] explored the phosphorus equilibrium between hot metal and low FeO containing slags and point out that phosphorus in slag exists as a phosphate ion and expressed the gas-slag reaction as equation 4. Their results showed that phosphorus partition increased with FeO concentration in slag and increasing basicity.

Basu et al. [26], [27] studied the partition coefficient between HM and CaO-SiO₂-FeO_x-P₂O₅-MgO slag system and concluded that slag basicity (expressed as wt. % CaO /wt % SiO₂) up to 2 has strong positive impact on the partition while the increase is much less pronounced with basicity after 2.5. Additionally, the phosphorus partition increased with FeO concentration up to 19 % wt. However, it became independent of FeO content beyond that and even decreased. They also found that increase of MgO content appears to reduce the phosphorus partition.

Turkdogan [28] upon re-valuating his assessment of P_2O_5 activity coefficients in molten slags found the lack of temperature dependency for P_2O_5 concentration of 0.2-1 wt % while it is a function of temperature above 10 wt.% of P_2O_5 in slag. Furthermore apparently, the weak dependency of P_2O_5 activity on MgO disappears at high P_2O_5 concentrations as indicated in the following equations.

$$\log(\gamma_{P_2O_5}) = -9.84 - 0.142((\%CaO) + 0.3(\%MgO)) \quad (10)$$

for 0.2wt. % < P_2O_5 < 1 wt. %

$$\log(\gamma_{P_2O_5}) = -\frac{34850}{T} - 3.85 - 0.058(\%CaO) \quad (11)$$

for 10 wt. % < P_2O_5

Earlier, Zhang et al. [29] had proposed using the Flood, Forland and Grjotheim [30] formalism which is based on the idea that molten slags are fully ionized. The formulation relates the equilibrium constant of a complex anionic reaction to molar fraction each cation species present in slag and equilibrium constant of the pure phosphates and activity coefficient being the logarithmic function of all activity coefficients. Basu et al. [31] also based on his review found better agreement to experimental data with ionic fractions of slag oxides.

$$\log(\gamma_{P_2O_5}) = -8.172X_{Ca^{2+}} - 7.169X_{Fe^{2+}} - 1.323X_{Mg^{2+}} + 1.858X_{SiO_4^{-4}} + 340/T + 11.6 \quad (12)$$

From the equation, it can be seen that increase in Ca^{+2} , Fe^{+2} and Mg^{+2} result in a decrease in activity coefficient of P_2O_5 whereas SiO_4^{-4} increases it.

Yang et al. [32] explored a thermodynamic model based on ion and molecule coexistence theory (IMCT) to analyse and predict phosphorus partitioning between CaO-SiO₂-FeO-Fe₂O₃-MnO-Al₂O₃-P₂O₅ and molten steel. The theory assumes that slag is composed of ions (Ca^{+2} , Fe^{+2} , Mg^{+2} and O^{-2}), simple molecules (P_2O_5 , SiO_2 , and Al_2O_3) and complex molecules of silicates, aluminates and others. All the ionic species take part in reaction by forming complexes of metal oxides (Me^{+2} and O^{-2}) which are in thermodynamic equilibrium with simple molecules. A large number of complexes were studied and it was found that the 3CaO. P_2O_5 and 4CaO. P_2O_5 complexes contributed to approximately 96 % and 4% of the measured phosphorus partition.

More recently, Assis [21] improved Suito's correlation based Suito's data [22], [33], Basu's data [31] and his own sets of an experiment in his dissertation. The model was based on the better agreement with experimental results, plant data for both EAF and BOF type slags for R^2 of around 0.94, a wider range of calcium, phosphorus, silicon and iron content of the slag. His final correlation is:

$$\log \left(\frac{\%P}{[\%P](Fe_t)^{\frac{5}{2}}} \right) = 0.073[(\%CaO) + 0.148(\%MgO) + 0.8(\%P_2O_5) + 0.113(\%SiO_2)] + \frac{11570}{T} - 10.403 \quad (13)$$

He also found that there is value impact of FeO as a reactant or possible oxidation of Fe from argon gas. It should be noted here that at high concentration of phosphorus in the hot metal (above 2 %) the distribution ratio will be written as (P)/[P]² since the phosphorus exists in the more stable dimer P₂O₅ instead of the monomer PO₄⁻³ at lower concentration where the distribution ratio is (P)/[P] [34]. It should also be noted that initial silicon content also has a significant influence on the dephosphorization efficiency. This is owing to the fact that silicon in the slag is usually present in SiO₄⁻² for in which 4 oxygen atoms form a tetrahedral structure. This forms networks and chains through bridging of oxygen atoms which effectively polymerizes the slag and thus increasing the slag viscosity. However, on the other hand, in highly basic slags, Ca⁺² and Mg⁺² promote breakages of these chains to form non-bridging oxygen which frees oxygen ions. This increases the oxygen activity in slag and thus promotes the dephosphorization [21]. This is often presented as ratio of non-bridging oxygens and free oxygen anions (NBO/T) which is basically ratio of mole fraction of the network formers species and network breaker species. It has been shown that increasing NBO/T increases the phosphorus partition as well [21]. So, it is important only to compare the distribution ratios of dephosphorization processes with similar initial phosphorus and silicon content as well as final concentrations of phosphorus.

Drain et al. [35], [36] has compiled and reviewed a large number of phosphorus partition correlations for different slag compositions and at different temperature ranges for oxygen steel making and also discussed the influence of additional factors such as TiOx load, heat duration and stirring rate.

All these studies have in common that CaO and FeO have a major part to play in dephosphorization while MgO has minor and SiO₂ affects it negatively. However, a slag basicity of above 2.4 and FeO content around 25 wt % is good to reach very low P levels. It should also be noted that oversaturation with CaO and MgO should be monitored to maintain slag viscosity. All these studies considered the liquid slag and liquid hot metal phases, however, owing to the multicomponent nature of slags, solid phases also play an important role to determine the rate and equilibrium condition for phosphorus removal. This will be explored in the next section.

3 Removal of Phosphorus

3.1 Blast Furnace

The blast furnace has been used for more than a couple of centuries as one of the most important methods to produce raw materials for steelmaking industry, as 93% of the total iron production for steel comes from the blast furnace. The main purpose of the blast furnace is to reduce the iron oxides to pure iron metal in a molten state while reducing the number of impurities for

example sulphur in the form of slag. Other products of the blast furnace include top gas mainly consisting of carbon monoxide, carbon dioxide, water, and hydrogen and flue dust. Blast furnace uses coal or coke as main reducing agents and heat sources with fluxing agents such as lime or limestone or BOF slag as slag formers in addition to sometimes self-fluxing¹ sinter or pellets. The main objective of blast furnace is to produce consistent hot metal (1480-1520 °C) with specification as Si (0.3-0.7%), Mn (0.2-0.4%) and P (0.06-0.13%). Figure 5. shows the typical blast furnace in working.

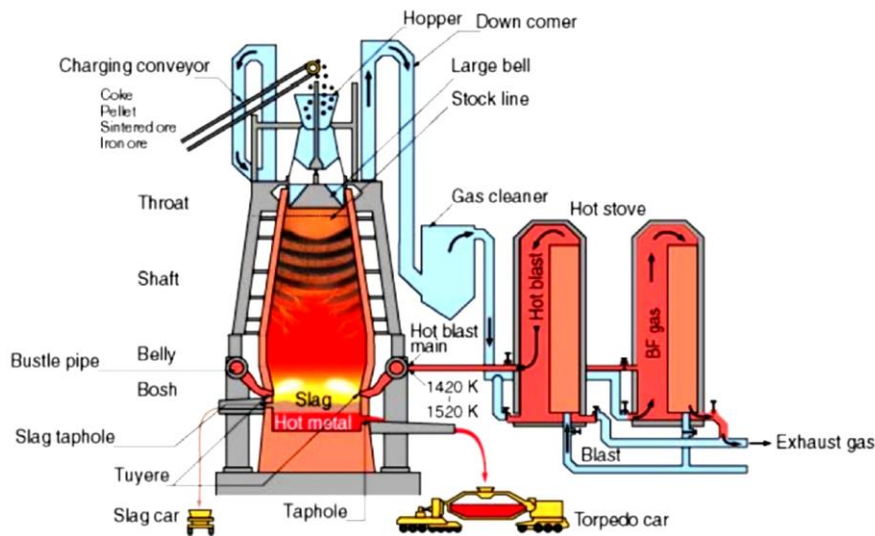


Figure 5. Typical blast furnace description

Dephosphorization

BF has primarily three zones for thermochemical reaction perspective: upper part (25-800 °C) for preheating and preparation zone, the middle part (800 -1000 °C) for indirect reduction and finally, the lower part (1000-1500 °C) for direct reduction and melting. However, for direct reduction of phosphorus, only the lower part is significant which starts from Bosh (See Figure 5.). Phosphorus, mostly originating from iron ore, converts to P_2O_5 gas owing to breakage of phosphate bonds with Silica present in the ore. Through the reaction, P_2O_5 is reduced by carbon in cokes and returns back to hot metal with 5-10 % loss in a gas. There is no phosphorus retention in the slag and the reaction is almost complete with no influence of physical and chemical condition. Reduction of phosphorus occurs in the following way in the blast furnace: [7]



¹ Self-fluxing: If the CaO/SiO_2 is so high (around over 1.2) that it gives desired basicity to BF (around 1.1), the agglomerate is called self-fluxing.

3.2 Primary Metallurgy

The primary metallurgy involves mainly converters and furnaces for major composition adjustments. The basic principle of converter steel making is to convert carbon rich iron source to steel by removal of various impurities through slag or as off gases. In converters, the basic raw material are either hot metal from BF and iron scrap (75% : 25%) for crude steel or steel scrap and direct reduced iron (DRI) in case of stainless steel making specially [7]. There are many types of furnaces based on the source of heat (chemical or electrical), combination of gas entry (oxygen only, or with argon and nitrogen) or arrangement of the gas entry (top blown, bottom blown or both) though there are some other specialized configurations including those with gaseous/liquid hydrocarbon cooling, steam addition and some with entry of coke and coal (allothermal processes). This report will primarily focus on the following technologies:

1. Basic oxygen furnaces (BOF) (mixed blown)
2. Electric arc furnaces (EAF) (bottom blown) coupled with Argon-Oxygen Decarburization (AOD)

The idea of keeping these tech in focus was to keep the report relevant for our partner participants SSAB and Outokumpu systems in this project.

3.2.1 Basic oxygen furnaces (BOF)

BOF is made of vertical vessel lined with basic refractory; it consists of parts namely spherical bottom, a cylindrical shell, and an upper cone. The main principle of BOF is to decrease the carbon content in liquid metal in order to produce desired steel. Typical properties of BOF is shown in Table 8. and Figure 6. shows the schematic diagram of working BOF [6].

Table 8. Typical properties of BOF.

Parameters	Typical Values
Specific working volume	0.65-0.75 m ³
Depth	1.2-2 m
BOF capacity	60-400 ton
Rotation	Horizontal
Oxygen flow rate	6–10 m ³ min ⁻¹ ton ⁻¹
Oxygen pressure	1–1.5 MPa
Service life of oxygen lance	150 heats
Service life of converter	400–600 heats

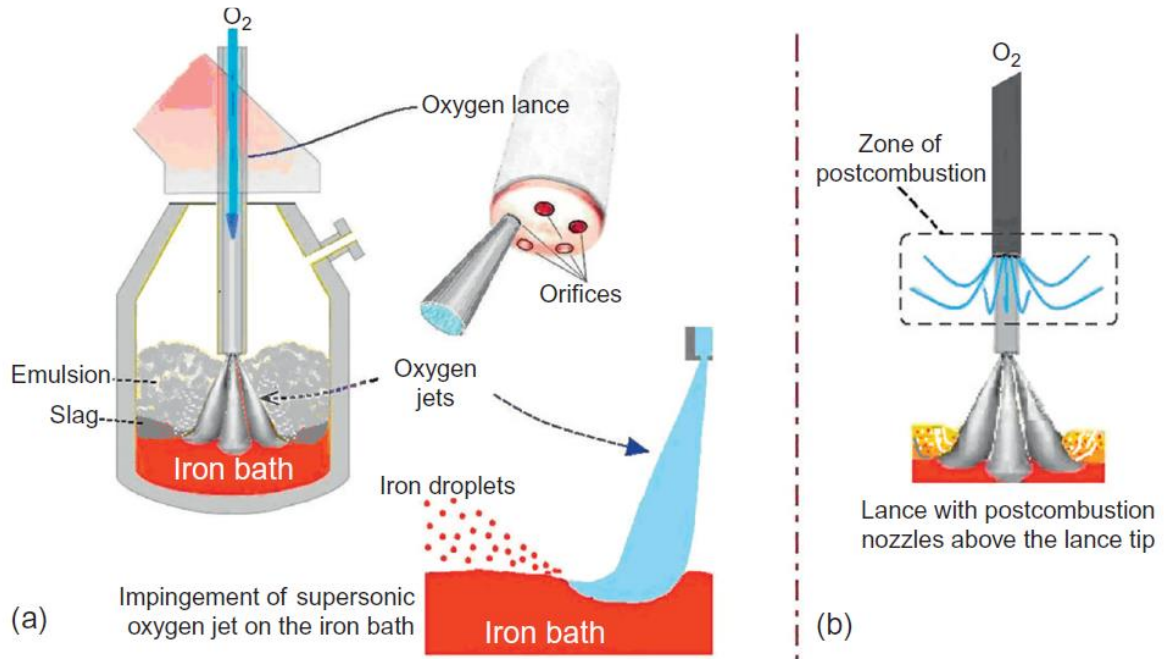
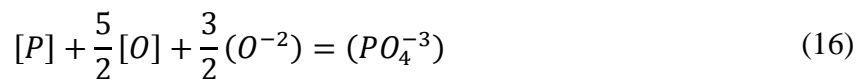


Figure 6. Schematic presentation of LD/BOF with: (a) a conventional supersonic lance and (b) a lance with post-combustion nozzles above the lance tip.

Dephosphorization

One of the essential impurity to be removed besides the decarburization of input carbon in hot metal is phosphorus. Similar to other constituents being oxidized such as carbon, silicon, Fe, Mn etc. phosphorus oxidation significantly depends on the mixing conditions, temperature and inlet composition of the hot metal. If the hot metal P concentration at the input is around 0.05-0.1 % dephosphorization is economical and reasonable in converter itself just as done at both SSAB and in an AOD converter at Outokumpu steel industries [2]. As discussed earlier in section 2 , the overall reaction of dephosphorization in ionic form can be described by the following equation:



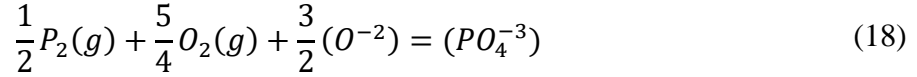
$$K = \frac{a(PO_4^{-3})}{a_P a_O^{5/2} a_{O^{-2}}^{3/2}} \quad (17)$$

Here it should be reminded that the round brackets () indicate concentrations in slag while square brackets [] indicate molten steel concentration. So clearly the equilibrium concentration of phosphorus in either the molten steel or slag will depend on the activity of oxygen in molten steel while another promoting factor is an activity of O⁻² in slag which is basically the slag basicity. The first factor (activity of oxygen in steel) depends on the following three factors:

1. The concentration of other metals or species in the feed hot metal
2. The temperature of the molten steel
3. Mixing type of converter

3.2.1.1 Impact of species in slag

It is important at this point to introduce an important term in dephosphorization known as phosphate capacity:



$$C_{PO_4^{-3}} = \frac{(\%PO_4^{-3})}{\left(P_{P_2}^{\frac{1}{2}}\right)\left(P_{O_2}^{\frac{5}{4}}\right)} = \frac{K_{dephos} \cdot a_{O^{-2}}^{\frac{3}{2}}}{f_{PO_4^{-3}}} \quad (19)$$

The phosphate capacity is a useful index since activity coefficients in slag are rather difficult to find but a useful estimate is based on the composition percentages and partial pressures of various participating components in the equilibrium level of phosphate ions. It indicates the degree of phosphorus absorption by the slag for the equilibrium between liquid slag phase containing phosphate anions, a gas phase containing oxygen gas and phosphorus vapour. Another important term here is the distribution ratio of phosphorus:

$$L_p = \frac{(\%PO_4^{-3})}{[\%P]} = \frac{C_{PO_4^{-3}} \left(P_{P_2}^{\frac{1}{2}}\right) \left(P_{O_2}^{\frac{5}{4}}\right)}{[\%P]} \quad (20)$$

The distribution ratio in simple terms means the distribution of phosphorus between slag and molten steel. Dephosphorization in steelmaking has been studied in two major pathways, first as liquid slag-liquid metal equilibrium and then also considering the solid phases in the slag involving lime and calcium silicate particles.

Phosphorus removal in BOF operation

In a typical top blown BOF operation, the hot metal is first transported from the blast furnace to BOF through torpedo vessels in Japan which sometimes lime and magnesium is added for desulphurisation and then the hot metal is poured into the furnace which takes around 5 mins. Usually, the metal scrap is added to the furnace prior to hot metal addition to avoid splashing. This is followed by oxygen blowing in three batches: (1) High lance height and low oxygen blowing to initiate oxidation (large metal dispersion) and heat generation reaction without touching the scrap, (2) Medium lance height and medium oxygen blowing rate for increased reaction rates and controlled slag formation (3) low lance height and high oxygen blow rate to promote optimum carbon removal. It should be noted here that most of the supersonic oxygen lances are designed for a single gas flow rate so it is not optimal to adjust the flow rate too much. However, variable top lance heads with possibility of different blowing rates are under development still.

The common flux components that are added include CaO as burnt lime and MgO as dolomite. CaO, as indicated earlier, plays a very important role dephosphorization, this will be detailed later in the section. MgO is usually added to minimize the wearing of the converter wall linings and CaF_2 is often added when there is low FeO content since it helps dissolve CaO particles in the slag. Often iron oxide pellets are added to both regulate temperature by cooling and to provide an initial concentration of FeO along with maintaining its concentration within the slag overtime [21].

During the BOF operation, once the hot metal is added onto metal scrap and the flux is added, rapid oxidation of the silicon and iron takes place to SiO_2 and FeO. As the blow continues, this iron oxide facilitates the dissolution of CaO solid particles into the slag in the form of calcium silicates which increases the basicity and mass of slag. This is followed by Decarburization of hot metal which produces CO gas that causes the slag foaming and also contributes in the reduction of FeO back to metal, however, over time the decarburization rate drops the FeO concentration in slag starts to increase again. The temperature of the hot metal increases steadily from 1350 to 1650 °C over the course of BOF operation and the slag temperature is usually 50 °C higher than hot metal [11], [37].

The dephosphorization rate in BOF depends significantly on the dissolution of a lime which in turn depends on the particle size of lime, its porosity, slag composition and the degree of saturation of dicalcium silicate [37]. Suito and Inoue [38] explored the phosphorus partitioning between liquid slag, lime and dicalcium silicate particles. They observed that in absence of prior phosphorus content in slag, the phosphorus distribution between dicalcium silicate and slag varied between 2 – 70 ratio with increase FeO content and slag basicity, however, the effect of temperature was quite weak. However, in a CaO- FeO- SiO_2 - P_2O_5 system, CaO particles were rapidly encapsulated by $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ without a P_2O_5 formation between the particle and the layer. This indicated that CaO did not directly influence dephosphorization in solid form but only the silicate form participated in the reaction [39].

Kitamura et al. [40] also explored whether adding lean calcium silicate particles contributed to dephosphorization. They proposed two pathways: first precipitation of $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ from liquid slag after phosphorus transfer to slag and second route is diffusion of phosphorus to precipitated calcium silicate particles. It was observed that the precipitation route was much faster than the diffusion route and thus, having prior dicalcium silicates do not necessarily improve phosphorus removal. The dephosphorization is effected greatly by lance height, formation of metal particles, and their corresponding residence time. The residence time of typical metal particle in the three-phase emulsion at a certain lance height has been explored both just by ballistic approach [41], which showed a pretty low residence time of 1 sec which was too low for any significant reaction, and by a gas “halo” formation approach, which included the evolution of CO through decarburization and thus increasing the residence time up to 200 secs in both Fe-C and Fe-C-Si slag systems [42], [43]. It was also observed that the phosphorus content of metal droplets is usually lower or equal to bulk bath indicating that the process is driven by metal droplets present in the slag/metal emulsion rather than in the bulk bath [44]. Additionally, it was also observed that phosphorus removal in metal droplets is faster than the Decarburization owing to the gas-halo system with high residence time and contact with oxidizing slag but depends on the droplet size.

Based on the above discussion, the desphosphorization mechanism in BOF includes:

1. Early in the oxygen blowing, when the oxygen lance is high, significantly good droplet ejection occurs that accelerates the phosphorus removal
2. Along the follow up of the blowing process when decarburization starts, CO starts forming which reduces FeO and thus reduces the oxidation potential of the slag. This may results in phosphorus reversion, especially if there isn't enough lime dissolution to retain phosphorus in the slag.
3. Near the end of blowing, the decarburization rate slows down and FeO content starts increasing again but often it's not enough to recover the possible reversion that has happened earlier.
4. Addition of FeO in form iron ore facilitates to maintain good FeO content to continue the phosphorus oxidation in parallel to the decarburization.

Kinetics of Phosphorus Removal

Phosphorus removal itself is not an equilibrium process owing to oxygen potential medium of the reaction being farther away from equilibrium owing to competing for side reactions. Thus, besides the phosphorus equilibrium, it's essential to explore the kinetic behaviour of phosphorus removal. Upon contact with P carrying iron with slag, the following set of steps occur [21]:

1. Mass transfer of [P] and [O] to slag- metal interface.
2. Mass transfer of $[O^{2-}]$ in the slag phase towards the slag-metal interface
3. Chemical reaction at the interface to form (PO_4^{3-})
4. Mass transfer of the formed phosphate away from the interface.

Owing to the high temperatures in the converter, the chemical reaction is usually expected to be lot faster than the mass transfer of individual entities within their respective mediums assuming that there is no phosphorus absorbing solid phase present (which as mentioned in the last section, even in the presence of solid CaO, isn't significant factor). It was also observed [45] that one of the main challenges in studying the process is identifying the driving forces for the reaction owing to the non-equilibrium oxygen potential at the interface. This is because of the decarburization in the metal phase which reduces the oxygen potential there thus at the interface there is high potential in the slag and low oxygen potential in the metal phase.

Monaghan et al. [45] performed an experiment on phosphorus carrying carbon saturated iron and slag. They found a first order kinetic rate for phosphorus concentration and also observed that FeO concentration changes the mass transfer coefficient of slag owing to decrease in viscosity however, it may affect the driving force of reaction both positively or negatively based on the direction of transfer. They thus also concluded that mass transfer in slag was the limiting factor. They proposed the phosphorus content change in slag be described as:

$$Q \left(\frac{d[\%P]}{dt} \right) = - \frac{k_s \rho_s A}{W_s} ((\%P)_i - (\%P)_b) \quad (21)$$

While the equilibrium equation can be rewritten as:

$$Q \left(\frac{d[\%P]}{dt} \right) = \frac{k_s \rho_s A}{W_s} \left(\frac{[\%P]_o}{[\%P]_e} \right) ([\%P]_b - [\%P]_e) \quad (22)$$

$$L_p = \frac{(\%P)}{[\%P]} \quad (23)$$

$$\left(\frac{[\%P]_o}{[\%P]_e} \right) \left(\frac{W_s}{\rho_s A} \right) \ln \left[\frac{[\%P]_b - [\%P]_e}{[\%P]_0 - [\%P]_e} \right] = -k_s t \quad (24)$$

Here, Q is the weight ratio of metal and slag, subscripts _b and _i indicate the concentration in bulk and interface respectively, k_s is the mass transfer coefficient, and W_s is the weight of slag while ρ_s is its density. Fruehan and Manning [46] assumed the reaction to be fast and at equilibrium and observed that oxygen potential at the interface was controlled by slag since there is no decarburization occurring at the interface. By using the mass conservation equation of phosphorus and thermodynamic equilibrium at interface, they formulated the following model.

$$\frac{\delta[\%P]}{\delta t} = -\frac{A \rho_m k_m}{W_m} \frac{1}{\frac{\rho_m}{k_s \rho_s L_p} + \frac{1}{k_m}} \left[[\%P] - \frac{\%P}{L_p} \right] \quad (25)$$

$$k_0 = \frac{1}{\frac{\rho_m}{k_s \rho_s L_p} + \frac{1}{k_m}} \quad (26)$$

And based on the mass balance at the interface and integrating the above equation

$$-A_T k_0 t = \frac{W_m}{\rho_m} \frac{1}{1 + \frac{W_m}{L_p W_s}} \ln \left[\left(1 + \frac{W_m}{L_p W_s} \right) \frac{[\%P]}{[\%P]_0} - \frac{W_m}{L_p W_s} \right] \quad (27)$$

Where A_T is the total surface area while subscripts m, s and 0 are metal, slag and initial conditions. They observed that the RHS increased initially but slows down as the reaction proceeds forward. It may be owing to either mass transfer coefficient decreases, the surface areas decreases or both. They proposed that the mass transfer coefficient is the function of mass flux of active element, which in this case was oxygen and as the reaction rate increases, the oxygen mass flux increases which causes spontaneous emulsion formation at the interface and thus decreasing the surface tension and increasing the surface area available. Gaye et al. [47] observed that the equilibrium interfacial tension was a function of oxygen and sulphur content while there was little impact of the slag composition. However, CaF_2 and Na_2O tend to increase the surface tension while presence of MnO decreases the surface tension. Gaye et al. [47] also observed that in the beginning the interfacial tensions starts decreasing as reaction proceed and when the interfacial tension completely vanishes or reaches extremely low values then the

reaction rate is maximum. However as the reaction starts slowing down, the interfacial tension achieved its equilibrium values quickly as well. So they concluded that when oxygen flux is more than $0.1 \text{ g atom m}^{-2} \text{ s}^{-1}$ the interfacial tension approaches zero and when it is lower than $0.01 \text{ g atom m}^{-2} \text{ s}^{-1}$ the tension achieves the equilibrium value.

3.2.1.2 Effect of Temperature

The second important factor is temperature of the molten metal. Dephosphorization reaction is overall exothermic thus slag dephosphorization capacity decreases with temperature [21], [22], [28] as can be seen in the Figure 7. High B and Low B indicates the high and low basicity of slag respectively. Here it can be clearly seen that temperature has much stronger impact on the distribution ratio than even the slag basicity (which will be discussed later in this section). That is why it is often preferred to have lower temperature for the dephosphorization which is usually not possible in a converter and thus dephosphorization is more favourable before the converter. This coupled with high oxygen activity at reduced temperature (lack of competitive reactions) significantly influences the distribution ratio positively if done before the converter. Nonetheless, this can still be managed well in a converter if the phosphorus concentration is rather low (0.05%-0.1%).

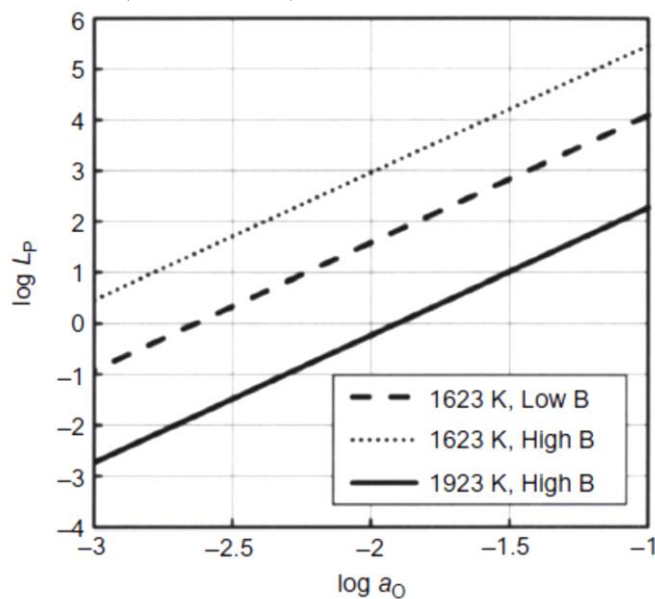


Figure 7. The effect temperature and slag basicity on phosphorus distribution ratio [2]

3.2.1.3 Effect of Mixing

In terms of converter mixing, the top blown reactor tends to oxidize more of the metals than the equilibrium would require owing to over-oxidation of steel bath surface. However, a bottom blown converter gives enough time to the oxygen bubbles to reach equilibrium and thus, the constituent oxide concentration mostly remain near equilibrium in bottom blown converters. However, in the AOD as discussed later, the conversion rate increases owing to both processes continuing simultaneously. Nonetheless, owing to the competitive series of transitory reactions with influence of high silicon and carbon concentrations, the activity level of oxygen is low in the molten steel and this coupled with the requirement of the having high

basicity in slag, most of the phosphorus conversion happens at interface of molten metal and slag called the permanent reaction [2], [48]. Additionally, the FeO activity significantly increases the oxygen activity at the interface and the presence of the non-equilibrium condition at the metal liquid interface facilitates high dephosphorization rate. (The equilibrated oxygen activity with the carbon content (around 6×10^{-4} is usually too low to produce high distribution ratio). Thus, in comparison of results from various types of converters, in case of high carbon initial content (0.3-0.1 % C) dephosphorization is higher in the top blown or combined blowing converters (e.g. AOD) than in bottom blowing process. However, at low carbon level below 0.1 % , higher dephosphorization may actually happen in bottom blowing converters since then oxygen activity is no longer the controlling factor but just the mixing effect is more significant [49].

Hot metal dephosphorization within converter sometimes requires specialized processes for effective phosphorus removal especially in the case of low basicity slag. One of the specialized processes is the traditional double slag process. The process is usually performed at lower temperature and high carbon content utilizing the permanent reaction under low basicity slag conditions and high iron oxide conditions. Usually a stand by converter or a continuous dephosphorization and decarburization process using the intermediate deslagging technique (MURC: Multirefining converter) is used [50], [51]. In the double slag process, the dephosphorization is carried out first at lower temperature followed by de-P slag removal and then decarburization. In MURC however, the dephosphorization is followed by slag removal and then decarburization just like in double slag but then the crude steel is removed and the de-C slag is recycled for the next round of charging. The Figure 8. demonstrates the typical set of changes in a MURC operation.

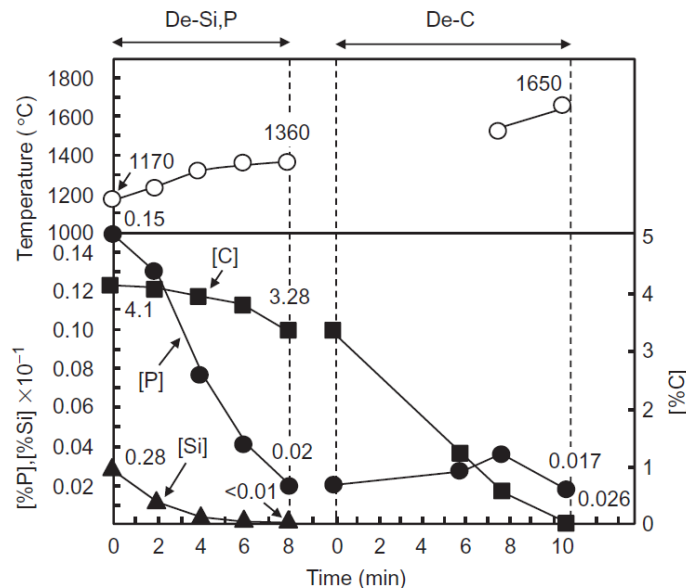


Figure 8. Changes in composition and Temperature during MURC process[50]

3.2.2 Electric Arc Furnaces (EAF)

An electric arc furnace usually takes in almost 100 percent of steel scrap or up to 15 % DRI or hot metal. Most of the electric arc furnaces use alternate current (AC) however, since late 1990s there has been an active interest in development of direct current EAFs owing to lesser electrode consumptions, less energy consumption and less flickering though higher specific costs, higher losses and excessive maintenance. This switch of focus highlights some of the core challenges in EAF converters: high consumptions, higher maintenance and higher costs as compared to BOF counterparts. The Figure 9. shows the development of EAF technology over time.

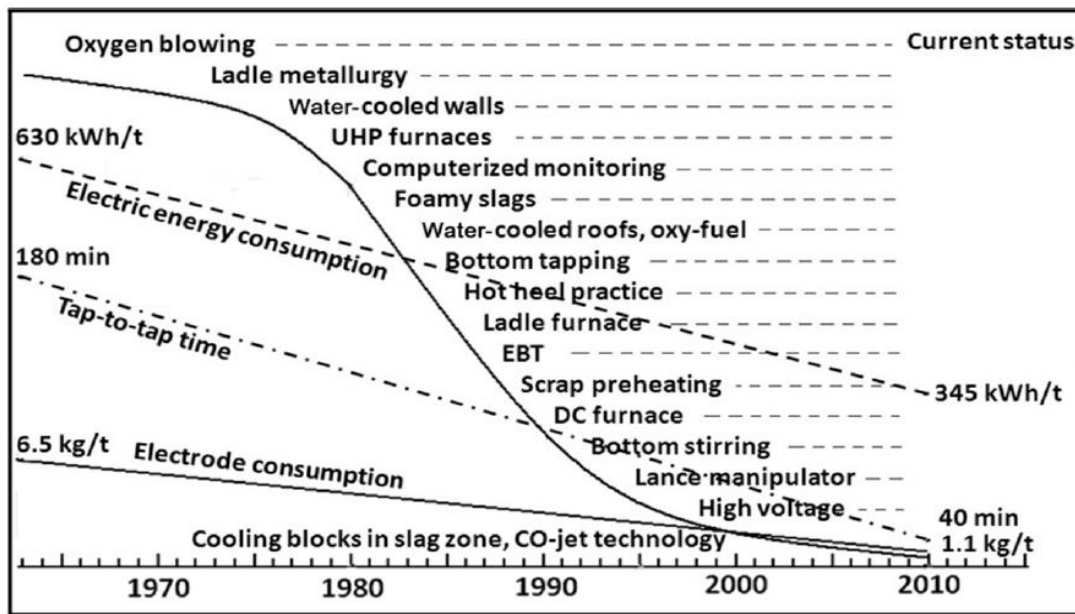


Figure 9. Evolution of EAF technology [52]

Despite the limitations, EAF is expected to have more significant proportion of future steel making especially owing to the fact that it can handle almost 100% steel scrap and with good control over emissions. According to International Energy Agency (IEA), the EAF is expected to have almost 50% contribution in steel making by 2050 as shown in Table 9.

Table 9. Scenarios of average global temperature increase and its influence on process route and consumption of metallic for year 2050 [53].

		Global Temperature Rise						
		Year 2010	Year 2050: Low Demand			Year 2050: High Demand		
			6 °C	4 °C	2 °C	6 °C	4 °C	2 °C
Process routes	EAF	28.5%	50.2	51.6	50.6	50.4	51.7	51.0
	BOF	71.5%	49.8	48.4	49.4	49.6	48.3	49.0
Metallics	Hot metal /pig iron	68.6%	45.6	44.3	40.8	45.5	44.2	37.9

Gas-based DRI	3.5%	7.0	7.0	9.5	7.0	7.0	9.7
Coal-based DRI	1.3%	4.8	4.8	0.0	4.7	4.7	0.0
Smelting reduction							
DRI	0.0%	0.5	0.5	4.8	0.4	0.4	7.4
Scrap	26.6%	42.1	43.4	44.8	42.4	42.4	45.0

EAF is commonly installed in two configurations: duplex and triplex. The former involves EAF installed before an argon oxygen Decarburization unit AOD where EAF melts the scrap, ferroalloys and other raw materials into liquid steel while AOD receives the charge of chromium and nickel and carbon content is adjusted. The other alternative is the triplex process which basically involves EAF steel making followed by converter refining and vacuum refining. This process usually takes longer and is less flexible in terms of raw materials but very low carbon and nitrogen specifications can be achieved by it. Furthermore, having a VOD in the final stages of the Decarburization reduces the risk of excessive chromium oxidation and low argon consumption as compared to the duplex process.

EAF can act as a fast “melting machine” and it operates as a batch process. EAF operates as cycle namely tap to tap cycle which consists of (i) charging of the furnace, (ii) melting phase, (iii) refining phase, (iv) de-slagging operation, (v) tapping of liquid steel, and furnace turnaround. EAF usually use scrap metals by heating it with high voltage electricity in a very short period of time with time ranges up to 40-50 min [54]. Figure 10. shows the working of EAF.

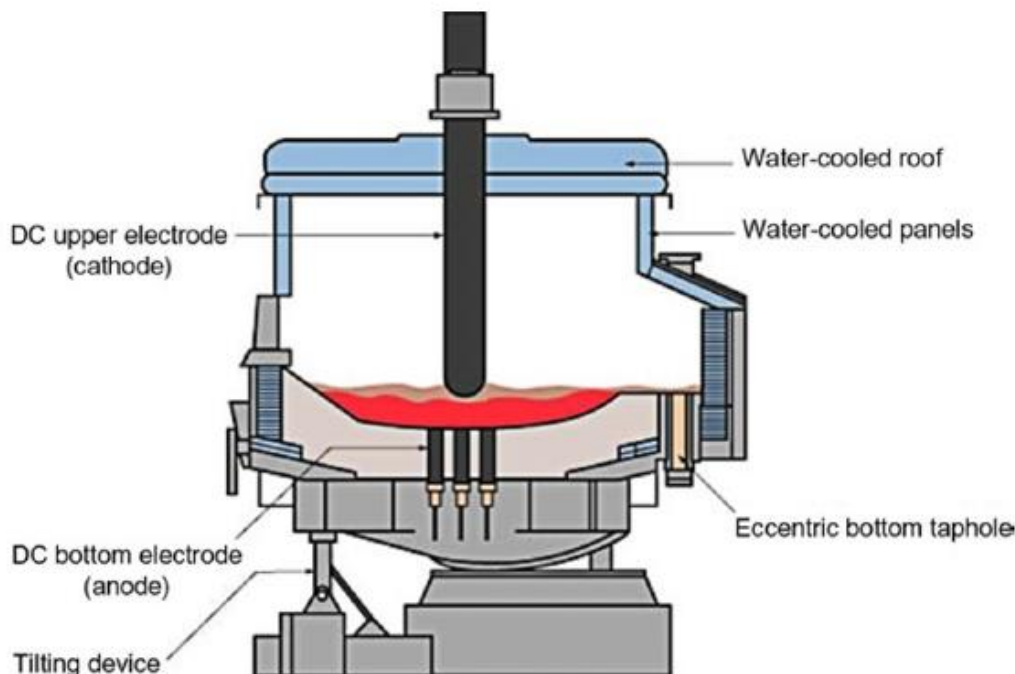


Figure 10. EAF with one electrode and bottom anode

Dephosphorization involves a metal-slag reaction between steel baths to the slag phase. In scrap-based EAF process, phosphorus concentrations are very low but for a DRI-EAF(Direct reduced iron-EAF) process, it can vary based on the source and composition of iron ore used

in the process and can elevate up to ~0.1% [55]. Furthermore, there is no pre-treatment in EAF and post-processing involving ladle furnace with low FeO concentrations are not suitable for dephosphorization. The total amount of phosphorus removed in the EAF depends upon key factors such as: calcium and iron oxide activities, initial phosphorus concentration in the DRI/scrap, temperature, slag volume, steel-slag mixing intensity, slag volume and type of flux added [11], [56]. Injection of oxygen in the bath contributes the refining of metal and forms phosphorus oxide in the slag. High oxygen activity is especially required in case of high carbon steel being introduced as scrap since carbon competes with oxidation of phosphorus just as in the case of BOF. The process can be optimized by adding CaO/SiO₂, which increases the slag basicity [11], [57]. Thus, higher content of CaO accelerates the dephosphorization process in presence of FeO by dissolving the phosphates, however, excessive CaO has adverse effect on the final quality of steel owing to retention of undissolved flux particles which in turn causes agglomeration or increased slag viscosity. The later, just like in BOF, reduces the mass transfer between slag and metal. Higher FeO content favours dissolution of CaO at lower temperatures, and therefore, FeO acts as a diluting agent for CaO at very high concentration thus, lowering its ability to bond with phosphorus; Furthermore, higher FeO contents also leads to lower Fe yield owing to its loss to slag unless additional FeO is added in the flux [58].

The effect of temperature on the dephosphorization is stated extensively in earlier sections: lower temperature favour the reaction and thus, higher dephosphorization occurs early on the process. Furthermore, hot heel i.e. the remaining metal and slag from previous heat, since oxygen can be lanced into the bath at low temperatures in that stage though if P-content is high already in the heel, it may cause P-reversion.

Another process of enhancing is dephosphorization is slag replacement: removing the slag when the dephosphorization - rate starts to fall and adding new slag, thus, propagating the reaction further [59] .

One of the distinct components in EAF is the presence of alumina. Alumina is present in steel making slags with 3-7 wt.%, where it comes from gangue in DRI, scrap as well as from flux. However, the impact of alumina on dephosphorization is rather inconclusive. It has been demonstrated in some studies in highly basic environments that dephosphorization rate increases in the presence of alumina owing to reduction of slag fluidity in concentrations lower than 5% [60]. Additionally, an increase in alumina concentration from 5-15% would result in 50% increased phosphorus holding capacity thus improving removal rate [56]. However, the basicity in EAF is quite much lower than the basicity in BOF. Tayeb A. [57] observed that in low basicity slag (CaO/SiO₂ < 2), alumina concentrations less than 10 wt% tend to decrease the dephosphorization ability of slag by more than half and it is more significant in EAF than BOF. He observed that an introduction of 5wt% alumina into with low basicity slag with other factor maintained constant, decreased the activity of FeO by 20% and caused a phosphorus partition reduction by a factor of 1.5. He also observed that alumina plays a strong network-forming roll which elongates the silicate polymerization structure (Refer to Section 2 for details on silicate polymerization) by forming [AlO₄⁻⁵]-tetrahedra unlike FeO and CaO being the chain breakers. This indicates that alumina not only decreases dephosphorization rate because of the increase in slag viscosity but also by reducing the free non-bridging oxygen to oxidize phosphorus. This effect cancels the cation's impact as a chain breakers and will form calcium

aluminates instead. Here in case of high silica content, alumina acts as an acid however, if the silica content is low, the alumina can act as a network modifier instead $[\text{AlO}_9]^{-9}$ -octahedral. However, it has been observed that such conditions are rather rare in EAF [57] and even if it exists, the impact of alumina will be merely as an diluting agent which makes more CaO available for breaking silica bonds though the effect on dephosphorization is still negative.

3.2.3 Converter metallurgy of for Stainless Steelmaking

In stainless steel making, chromium is added to steel for its unique contribution to high corrosion resistance in steel. The unique corrosion resistance introduced is owing to a passive oxide layer that is formed at the surface the iron steel which protects the carbon steel underneath from oxidation and the layer is also self-repairing under right conditions. Since it's patenting, there have been many forms of stainless steel been prepared based on the crystal structure ranging from austenitic steel (with nickel, manganese and nitrogen), ferritic (owing to magnetic properties of alpha iron with Mo, aluminium and titanium additives), martensitic (similar to ferritic in composition but higher Mo content) and duplex (having both austenitic and ferritic structures with different additives).

During the manufacturing of stainless steel in converters, having high carbon coupled with chromium is a problem owing to the oxidation of both at similar conditions which called sensitization. Thus, in the older times, stainless steel was only produced by stainless steel scrap and carbon steel scrap melting in an EAF and that followed by Decarburization till 0.08% C by oxygen at chromium level of 10-14% which raised the temperature up to 1800 °C. This high temperature lead to prioritization of carbon oxidation instead of chromium which has weaker oxidation capacity at higher temperatures. Any part of chromium that is oxidized is then reduced by using silicon and then by aluminium. This was followed by addition of Fe-Cr additive to adjust the chromium concentrations, however only low carbon Fe-Cr ore can be used which is relatively much more expensive and additionally higher chromium content of 65-75% was required however, nowadays only 50-55% Cr content is typical in the “charge chrome”. The invention of AOD revolutionized stainless steel making since it facilitated the usage of high carbon Fe-Cr ore owing lowered partial pressure of CO that is formed in the presence of argon [61].

3.2.3.1 Argon- Oxygen Decarburization (AOD) Converter

Figure 11. shows the schematic diagram of an AOD Converter. AOD converter is used for the production of stainless steel, the hot liquid crude steel is transferred to the AOD-converter for further refining after melting. The melt is decarburised using oxygen, nitrogen, and argon and the reduction of slagged chrome happens in converter. Desulphurisation is carried out, depending on the steel grade, before the final temperature and alloy is set. In order to achieve an optimum of maximum Decarburization and minimal slagging of Cr, an argon-oxygen mixture is injected by means of a lance or bottom blowing. The ratio of argon to oxygen alters according to the duration of the refining process [62] .

Advantages:

- Maximum Decarburization with minimized Cr oxidation
- Minimal slagging
- N - removal

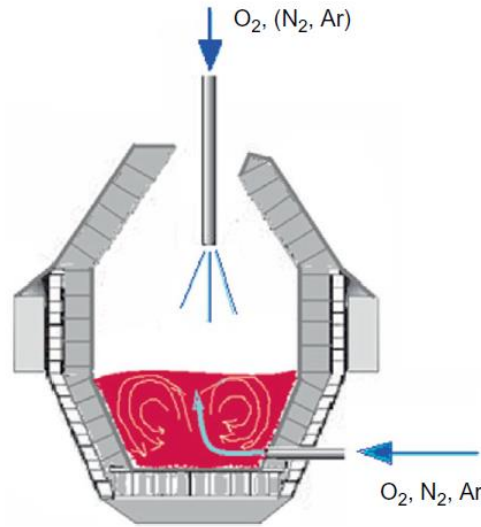


Figure 11. Scheme of AOD converter [6]

Dephosphorization in AOD

Dephosphorization of crude steel coming either from BOF or EAF into AOD is considered more challenging especially in the duplex arrangement. Based on the conventional understanding of dephosphorization process in BOF, dephosphorization in AOD is affected by the following parameters in general:

- Composition of molten iron and slag
- Slag basicity
- Temperature

In the AOD Process, just like mentioned in the BOF section of this report, the temperature and slag basicity plays an important role in dephosphorization. Low temperature, and high slag basicity improves the dephosphorization rate significantly [63]. The basicity of slag in AOD is defined as the ratio between the basic oxides and acid oxides present in the slag.

$$\text{Basicity} = \frac{\text{CaO} + \text{FeO}}{\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{P}_2\text{O}_5 + \text{Cr}_2\text{O}_3} \quad (27)$$

So, CaO is the most significant element for dephosphorization since it increases the basicity of slag and its product $4 \text{ CaO} \cdot \text{P}_2\text{O}_5$ is stable at higher temperature during steelmaking. However, other than basicity itself, the viscosity of slag plays an important role since it affects the mass transfer across the slag-metal interface and uneven melting of CaO particles leads to an increase in slag viscosity which ultimately results in lower dephosphorization. Dissolution of CaO in the slag is also increased by the FeO content, however, if FeO content increases to a higher level it reduces the CaO in the steel making [64].

The conventional dephosphorization processes involving oxidation of phosphorus as stated here based on the equation 4 has some major concerns when applied to AOD. The most important one is owing to the presence of chromium which oxidizes in preference to phosphorus owing to the overall chromium oxidation reaction as follows:

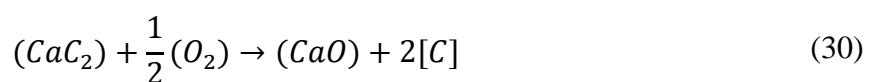


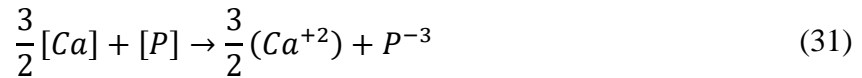
Based on the comparison of equation 4 and equation 28, it can be seen that as chromium content keeps on increasing, the prevailing oxygen partial pressure decreases and thus, rendering the dephosphorization more difficult. However, using highly basic oxides in slag can help the dephosphorization reaction at lower oxygen partial pressures. The slag basicity is also impacted by the high content of chromium as it forms an amphoteric oxide just like Alumina in the slag. Since the slag is primarily basic, these oxides act as acidic oxides and reduce the actual basicity of the slag so for slag basicity higher than 2, chromium acts as chromate ions) CrO_4^{-3} while at lower basicity, it stays in the cationic form of Cr^{+2} . Thus, high chromium content decreases dephosphorization rate however basic oxides such as CaO, Ba_2O and CaF_2 (which also decrease the surface tension of slag thus improving mass transfer) improves the phosphorus removal rate. Nickel behaves in a similar way as chromium in the process and negatively impacts the process. High CaO content also reduces the chromium losses overall [63].

Thus, slags commonly used for the oxidation of phosphorus pathway are a combination of oxides (CaO, BaO, Na_2O etc.) or halides (CaF_2 , $CaCl_2$, $BaCl_2$ etc.) and oxidants (Cr_2O_3 , $CaCrO_4$, Fe_2O_3 etc.). The halides especially tend to lower the viscosity of the slag, decrease the activity coefficient of P_2O_5 and raise the activity coefficient of Cr_2O_3 . Furthermore, increasing carbon content between 2-4 percent tend to decrease the activity of chromium and thus, the oxidation of chromium [65] and increase the phosphorus activity however, the key to have sufficiently lower phosphorus concentration is to keep the temperature rather as low as possible [66].

According to Karbowniczek et al.[63], the initial carbon content also has significant direct influence on dephosphorization. Too low carbon content (less than 2 %) increase chromium losses to the slag owing to preferential oxidation of chromium. Moderate carbon (2-4 %) enhances the dephosphorization rate as it reduces the melting point of molten iron, thus allowing for lower temperature of the process. However, too high carbon content decreases the dephosphorization rate as it decreases the oxygen potential in the metal. Effective dephosphorization is only possible at lower temperature and high oxygen potential.

Another strategy is by the pathway of reduction of phosphide instead of oxidation to phosphates. This involves using molten Ca and CaC_2 - CaF_2 to reduce the partial pressure of oxygen sufficiently low as indicated by the following equations:





Harashima et al. [67] demonstrated how the carbon content increases when calcium carbide, dissolved by CaF_2 , dissociates and increases the calcium content of hot metal. This is accompanied by reduction of impurities of the group IV, V and VI in the periodic table especially phosphorus, nitrogen and sulphur as shown in Figure 12. These reduced species get dissolved in the slag and then, when the oxygen blow starts to decarburize the hot metal, the phosphorus, now already in slag, oxidizes though independently of chromium this time. In this process, the upper limit of CaF_2 is around 25 percent since beyond that value, calcium preferentially reacts with the refractories or evaporates. [66] A major disadvantage of the process is the generation of the hazardous phosphine gas PH_3 when exposed to moisture in air thus, it is essential to oxide the phosphide in slag to phosphate by the addition of iron ore or by injection of oxygen and thus, it's quintessential for environmental reasons.

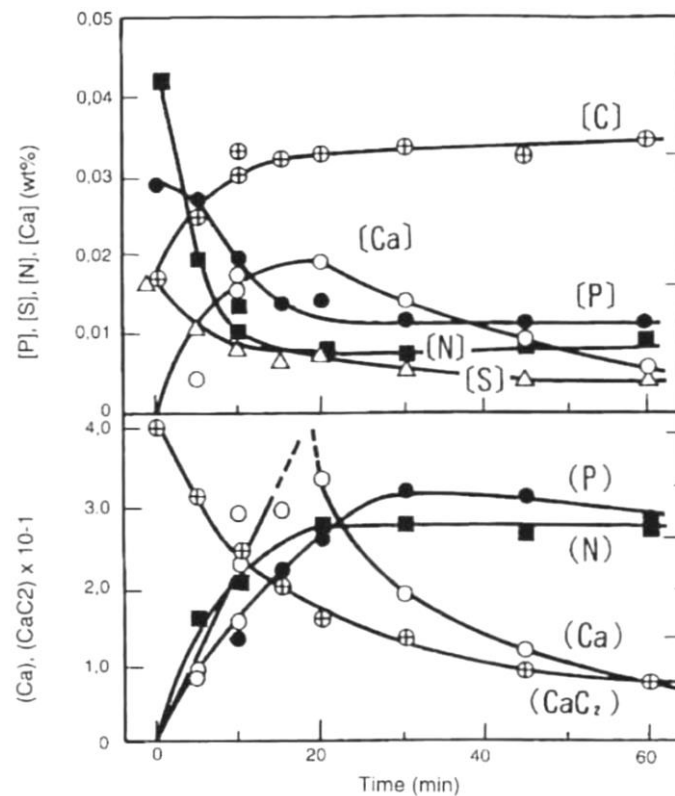


Figure 12. Change of hot metal and slag composition with the addition of 50% CaC_2 -50% CaF_2 on 18% Cr-8% Ni-0.5 % steel

Owing to significant impact of initial carbon and chromium content on dephosphorization, Sano et al. [66] proposed differentiating the various types of ores in terms of carbon content. High carbon-High chromium ferrochromium cannot be dephosphorized with any slag without excessive loss of chromium. However, medium carbon- high chromium alloy can incorporate the phosphide reduction process with dephosphorization by CaC_2 - CaF_2 . For carbon steel with carbon content of 0.5-6 % BaO - $BaCl_2$ is a suitable slag if chromium content is 22-30% however, if the chromium content is lower than 22 % and carbon is 3-6 % then a more suitable and economical candidate would be CaO , Li_2O_3 , NaO and K_2O . These recommendations are demonstrated in Figure 13.

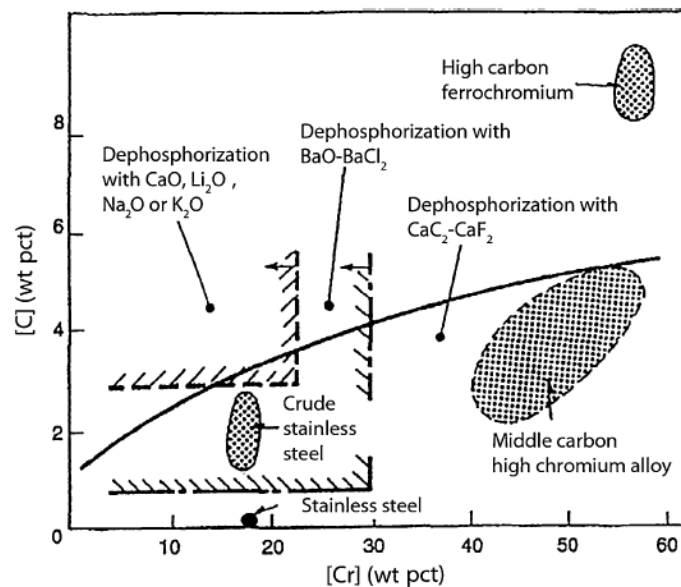


Figure 13. Suitable range of metal compositions for dephosphorization of stainless steel [66]

3.2.3.2 VOD

Vacuum oxygen decarburization (VOD) treatment is carried out under vacuum in a ladle containing crude stainless steel charge from either EAF, AOD or BOF. The ladle is placed in a vacuum chamber which is followed by argon stirring from the bottom and oxygen is blown by the lance at the top. Due to intensive mixing and vacuum, degassing of gases such as H_2 , N_2 and CO takes place followed by foaming on steel. VOD process is suitable for low carbon, low nitrogen ($C \ll 1\%$) crude steel which are difficult to achieve in an AOD. Usually, AOD and VOD are put in series in order to have better results. VOD Process have higher investment and operating cost but it requires lower argon consumption, lower impurity level, less silicon for slag reduction and de-oxidation [6]. The main difference here as compared to AOD is the usage of vacuum which allows for even lower CO partial pressure than possible in AOD and thus, facilitating production low carbon low nitrogen steel grades. However, most of the dephosphorization measure applicable are the same as AOD.

4 Concluding remarks

In steelmaking process, the phosphorus primarily acts as an impurity and has become increasingly important over the course of past few decades owing increased utilization of low-quality ores. Phosphorus in steelmaking primarily originates from the iron ore and in minor amounts from the additives such as fluxes and alloying ores in BOF pathway, however, in the EAF pathway, the major source of phosphorus would either be from scrap, the direct reduced iron (DRI) (if used), and alloying elements.

In BOF pathway, the dephosphorization is a bigger concern owing to high dependency on iron ore quality and minimal removal in the blast furnace, moreover, lack of utilization hot metal pre-treatment processes outside Japan. Based on the research, FeO and CaO are the core components involved in the dephosphorization in the BOF converter while other elements

either facilitating or hindering their capacity by either dilution, deactivation, agglomeration, increasing viscosity and changing slag melting point. Extensive research has been done in studying the phase equilibrium of complex phosphorus carrying slags, studying the impact of various parameters and other elements on the phosphorus partition and their behaviour in actual off-equilibrium conditions of industrial operation. One of the main topic worth mentioning exclusively is Imphos: improving phosphorus refining [44] which is a large European 4-year projects which provided extensive data through their pilot studies on the matter and thus, is a great reference for the topic.

In stainless steel technologies, especially duplex (EAF-AOD) and triplex processes (EAF-AOD-VOD), the phosphorus concentration is generally lower since there is no hot metal usage and mostly scrap is used as the raw material. Furthermore, there is larger temperature variation with lower temperatures in the beginning in an EAF where most of the phosphorus is removed owing to almost ideal conditions for the reaction though it is only hindered by mass transfer limitations with the flux and amount of time spent in lower temperatures or saturation of slag early on followed by phosphorus reversion of not replaced. However, there has been a recent trend of replacing of steel scrap by hot metal coming from iron-chromium ores which require more extensive dephosphorization. In AOD, the dephosphorization rather more problematic owing to the delicate balance of maintaining optimum chromium concentrations in the steel, addition of relatively high phosphorus alloying ores and higher temperatures but the process follows a similar pattern as a regular BOF converter for dephosphorization if considered to be at interfacial equilibrium.

Based on the report, there is extensive information available on phosphorus equilibrium but there is a larger level of uncertainty in the non-equilibrium behaviour of phosphorus in the presence of three phase systems in an actual industrial operation involving gas (top or bottom blowing oxygen), liquid (liquid metal and slag) and solid phases (undissolved flux/alloying ores and interaction with agglomerated remains from the previous heat at walls). Some of the research questions that were discovered during the review included:

1. What is the impact of presence of alumina, chromium and minor elements such as titanium oxides, nickel, cobalt etc. in three phase system, not just at equilibrium conditions?
2. What would be the upper limit phosphorus concentration that can be tolerated in BOF or EAF pathway and how the behaviour would change in case of phosphorus concentrations higher than 2-3 %, would it need specialized strategies such as hot metal pre-treatment to produce ultra-low-carbon stainless steel?
3. How to optimize the slag removal and recycle to facilitate in dephosphorization in case of high phosphorus hot metal and minimize the flux and iron losses, furthermore, to reduce the phosphorus reversion?
4. How the phosphorus removal can be enhanced outside the main converter such as EAF or BOF? For example how to maximize the dephosphorization either as hot metal pre-treatment or in secondary steelmaking such as AOD, CAS-OB (composition adjustment by sealed argon bubbling) or ladle furnace?
5. How entry of flux particles or powder through bottom blowing tuyeres would affects the dephosphorization process? Would it drive to be faster owing larger surface area available

for particles, high oxygen potential available, faster removal of slag from the reaction zone (in transitory reaction stage) and thus, facilitating phosphorus equilibrium to move forward, possibly reducing the phosphorus reversion if removed?

6. What are the alternative strategies for dephosphorization in a reduction environment in an AOD process for high-medium carbon ferrochrome ore?

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